

GRCop-84

A High Temperature Copper-based Alloy For High Heat Flux Applications

David L. Ellis

NASA Glenn Research Center

Cleveland, OH 44135

Abstract

While designed for rocket engine main combustion chamber liners, GRCop-84 (Cu-8 at.% Cr-4 at.% Nb) offers potential for high heat flux applications in industrial applications requiring a temperature capability up to approximately 700°C (1292°F). GRCop-84 is a copper-based alloy with excellent elevated temperature strength, good creep resistance, long LCF lives and enhanced oxidation resistance. It also has a lower thermal expansion than copper and many other low alloy copper-based alloys. GRCop-84 can be manufactured into a variety of shapes such as tubing, bar, plate and sheet using standard production techniques and requires no special production techniques. GRCop-84 forms well, so conventional fabrication methods including stamping and bending can be used. GRCop-84 has demonstrated an ability to be friction stir welded, brazed, inertia welded, diffusion bonded and electron beam welded for joining to itself and other materials. Potential applications include plastic injection molds, resistance welding electrodes and holders, permanent metal casting molds, vacuum plasma spray nozzles and high temperature heat exchanger applications.

Introduction

Cu-Cr-Nb alloys were initially examined under the United State's National Aeronautics and Space Administration's (NASA's) Earth-To-Orbit Program during the 1980s. Efforts during the 1990s and 2000s under various space programs have brought the alloy to commercial scale production. The desire was to develop an elevated temperature high strength copper-based alloy that retained most of the thermal conductivity of copper but which had creep and low cycle fatigue (LCF) lives that exceeded NARloy-Z (Cu-3 wt.% Ag-0.5 wt.% Zr), the Space Shuttle Main Engine (SSME) Main Combustion Chamber (MCC) liner. Initial results with lab scale runs (1 to 25 grams) using Chill Block Melt Spinning (CBMS) showed that adding 2 to 10 atomic percent chromium and 1 to 5 percent niobium at a 2:1 atomic ratio produced the high melting point intermetallic compound Cr₂Nb within a nearly pure copper matrix (1). Mechanical testing of the CBMS ribbons showed a considerable increase in strength at room and elevated temperatures for the Cu-Cr-Nb alloys (2). Based upon the balance of properties, the Cu-8 at.% Cr-4 at.% Nb alloy was selected for scale-up to commercial production.

The alloy was designated Glenn Research Copper 84 or GRCop-84. GRCop-84 has higher strength, creep resistance, LCF life than NARloy-Z while possessing a lower thermal expansion and thermal conductivity. GRCop-84 also exceeds the properties of most other competing alloys such as AMZIRC (C15000, Cu-0.15Zr), GlidCop AL-15 (C15715, Cu-0.3Al₂O₃) low oxygen grade, Cu-0.7Cr (C18200) and Cu-1Cr-0.1Zr (C18150). The benefits are generally increased substantially when comparing the alloys following a high temperature thermal exposure such as a braze cycle or diffusion bonding process.

Production

Cu-Cr-Nb alloys can only be successfully produced using rapid solidification technology. Conventional argon gas atomization was chosen because it offered a large industrial base, relatively low cost, volume production capability and a moderately high cooling rate. Elemental copper, chromium and niobium are melted to produce a uniform molten alloy. The molten metal is atomized to produce a fine powder. For extrusion and Hot Isostatic Pressing (HIPing), -140 mesh (<106 μm) powder is used. Typically this powder has a mean powder diameter between 30 and 40 μm. For Vacuum Plasma Spraying (VPS), a finer powder is desired. Both -270 mesh and -325 mesh (<53 μm and <44 μm) have been used with great success.

Three conventional consolidation techniques have been successfully used to produce GRCop-84. At NASA Glenn Research Center (GRC), direct extrusion of the powder to a round or rectangular shape and HIPing to simple shapes have been examined. Both consolidation methods produce fully dense material that has excellent properties. At NASA Marshall Space Flight Center (MSFC), VPS has been used to produce liners with an integral NiCrAlY inner layer and a functional gradient from the NiCrAlY to the GRCop-84 as the liner is built up from the inside to the outside. The sprayed powder was fully densified after spraying and HIPing.

Once the powder is consolidated, the alloy can be processed like any other high strength copper alloy. For liners, GRCop-84 has been successfully hot, warm and cold rolled, bump formed, stamped and metal spun. Tube drawing has been successfully demonstrated with tubes as small as 0.3 cm OD x 0.08 cm wall (0.125" OD x 0.030" wall). To support manufacturing of complex parts by stamping, bending and other techniques, forming limit diagrams for GRCop-84 at room temperature and 200°C (392°F) have been created (3). The usefulness of the forming limit diagrams was demonstrated by successfully stamping a complex part from flat sheet without significant thinning or any failures.



Figure 1 – GRCop-84 can be formed into shapes using conventional methods used for copper-based alloys. The cylinder shown on the left was bump formed into two half cylinders and friction stir welded together. Another cylinder was hot metal spun into the hourglass shaped liner preform shown on the right.



Figure 2 –GRCop-84 can be Vacuum Plasma Sprayed (VPSed) into complex shapes. NASA MSFC has successfully used VPS to produce many liner configurations including a full scale Space Shuttle Main Engine Main Combustion Chamber liner.

Vacuum Plasma Spraying has been successfully proven for both small and large liner fabrication (4, 5, 6). VPS has the advantage of being able to use a Functionally Graded Material (FGM) on the hot wall surface. This allows a gradual transition from pure NiCrAlY or other coating through a mixture of the coating and GRCop-84 to pure GRCop-84. The gradual transition eliminates the traditional sharp interface of overlay coatings and a prime potential failure point.

Microstructure

GRCop-84 contains 14 volume percent Cr_2Nb in a pure copper matrix. The intermetallic compound dispersion strengthens the copper matrix and refines and controls the copper grain size. Approximately two-thirds of the strengthening comes from a Hall-Petch mechanism while one third is from Orowan strengthening (7). The Cr_2Nb is extremely stable up to at least 800°C (1472°F). Because the Cr_2Nb particles do not coarsen, the grain size remains nearly constant and even long term exposures to temperatures under 800°C do not greatly degrade the strength of GRCop-84. Most other copper alloys suffer severe loss of strength when exposed to these high temperatures. Precipitation strengthened alloys such as NARloy-Z, AMZIRC, Cu-0.7Cr and Cu-1Cr-0.1Zr can have the strengthening phase dissolve and the grains grow extremely large. Some of their strength can be recovered by a subsequent aging heat treatment, but in a finished part such a heat treatment may not be possible.

Thermophysical Properties

Thermal expansion is a critical thermophysical property for rocket engine liners. Most stresses and strains are thermally induced rather than mechanically generated. Thermal expansion of the hot wall is typically 1% which creates plastic deformations and stresses while promoting low cycle fatigue (LCF) and creep as the engine is fired repeatedly.

GRCop-84 has a lower thermal expansion than any of the competitive alloys that have been examined. The decrease is almost 7% relative to pure copper in the hot wall temperature range. The lower thermal expansion directly translates into lower creep stresses and smaller LCF strain ranges. For a liner application, a 2X to 100X increase in life can be expected from the direct substitution of GRCop-84 for other copper alloys depending on the failure mechanism for the design.

Thermal conductivity is a key design factor for combustion chamber liner applications. This drove the decision to use precipitation and/or dispersion strengthening for the next generation of liner alloys. While materials such as stainless steel may have much greater strengths and temperature capabilities than copper-based alloys, their low thermal conductivity would result in much higher temperatures and probably melting when exposed to the multi-megawatt per square meter heat fluxes typical of rocket engines.

GRCop-84 has a thermal conductivity of between 305 and 320 $\text{W/m}\cdot\text{K}$ (176 to 185 $\text{BTU/h}\cdot\text{ft}\cdot^\circ\text{F}$) or 75% to 84% of the value of pure copper over the operating temperature range of a liner. This is comparable to NARloy-Z near room temperature but

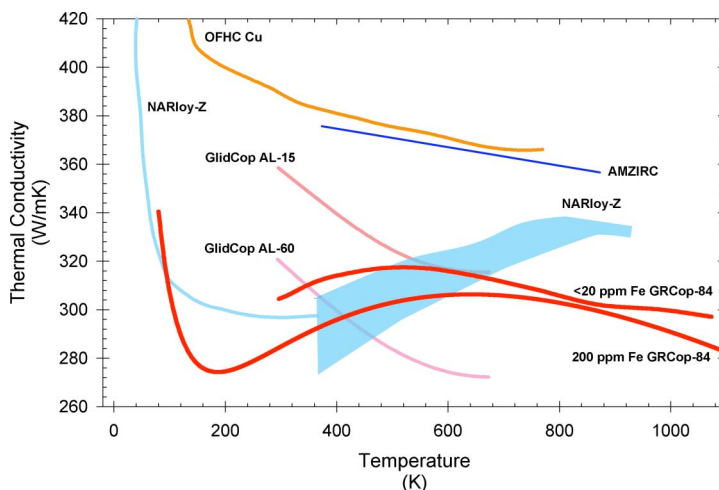


Figure 3 – The high loading of Cr_2Nb reduces the thermal conductivity of GRCop-84 compared to pure copper, but it still superior to most materials.

lower at higher temperatures such as those experienced at the hot wall. The lower thermal conductivity of GRCo-84 does result in an increase in temperature, but analysis for rocket engine applications indicate the increase is typically 35°C (65°F) or less. Given the nearly 200°C (360°F) increase in temperature capability of GRCo-84 over NARloy-Z, this small increase can be handled by GRCo-84 easily.

Iron from the chromium used to make the powder was determined to be detrimental to the thermal conductivity. As a result, the specifications have been changed to <50 ppm Fe required and <20 ppm Fe desired. This resulted in a significant increase in thermal conductivity at lower temperatures.

As part of the modified Kohlrausch thermal conductivity measurements, the electrical resistivity of GRCo-84 was measured from -186°C (-303°F) to 200°C (392°F). At room temperature the electrical conductivity of as-extruded GRCo-84 is 67% of the International Annealed Copper Standard (IACS).

Tensile Strength

GRCo-84 was optimized for usage between 300°C and 700°C (572°F and 1292°F). As a result, its low temperature strength is inferior to Cu-Be (C175xx) and most other precipitation strengthened copper-based alloys. However, unlike those alloys, GRCo-84 retains good strength to above 700°C (1292°F) while other precipitation strengthened copper-based alloys generally lose most of their strength between 300°C and 450°C (572°F and 842°F) (8, 9).

Another major advantage of GRCo-84 is its thermal stability. Once most other copper-based alloys are exposed to high temperatures, their strength remains low until they are given another precipitation heat treatment, and even this may not be sufficient to restore all of their mechanical properties. If as in the case of AMZIRC cold work is also used to strengthen the alloys, full strength cannot be restored regardless of the thermal treatment used after annealing occurs. In contrast GRCo-84 shows less than a 10% decrease in strength up to 700°C even after exposure to simulated braze cycles in the 935°C to 1000°C (1715°F to 1832°F) range.

Creep

Creep of GRCo-84 has been tested extensively between 500°C and 800°C (932°F and 1472°F) primarily in the as-extruded and as-HIPed conditions but more recently using production plate and sheet samples. The creep lives are one to three orders of magnitude longer than NARloy-Z tested at the same temperatures. Alternatively, for the same creep life, GRCo-84 can support approximately 15% more load than NARloy-Z. Similar benefits are seen over other copper-based alloys in this temperature range. Creep elongations at failure for GRCo-84 are typically 8% to 14%.

Low Cycle Fatigue (LCF) Lives

GRCo-84 exhibits high LCF lives at room and elevated temperatures. The lives are minimally influenced by temperatures up to 600°C (1112°F), the highest temperature tested, and simulated braze cycles have no discernable effect on LCF lives. The Cr₂Nb precipitates appear to retard or minimize the development of persistence slip bands and extend the life far above pure copper and most competitive alloys.

Joining

Limited joining experimentation has been conducted. Friction stir welding has proven to be an extremely robust joining method (10), but it is limited to joining GRCo-84 to itself. Tensile tests indicate that the welds typically retain over 90% of the base metal strength. Inertia welding has been used to attach 310 and 316 stainless steel ends on GRCo-84 LCF specimens. During LCF testing the samples failed in the GRCo-84 rather than at the weld joint. Electron beam welding has shown success in joining GRCo-84 to itself and has potential for joining to dissimilar materials. Limited brazing has been conducted, but it appears to be possible to braze GRCo-84 to a variety of materials using the same brazes used for other copper alloys. Diffusion bonding of GRCo-84 to itself has been demonstrated, and it can likely diffusion bond to other metals that are amiable to diffusion bonding with pure copper.

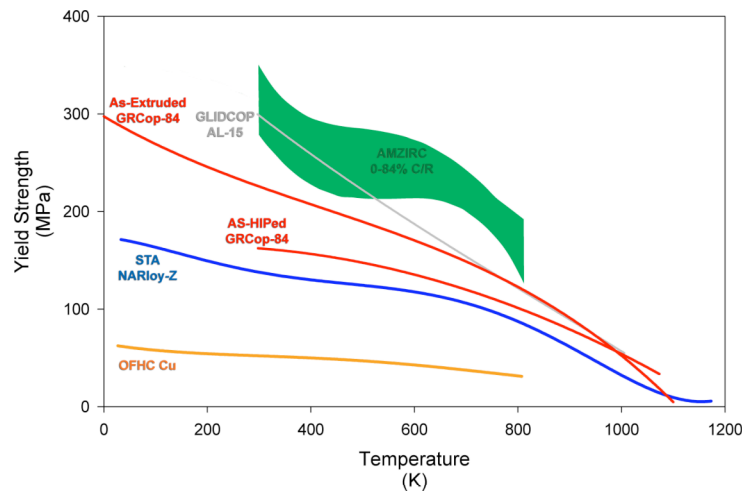


Figure 4 – Compared to other copper-based alloys, GRCop-84 in either the as-extruded or HIPed condition is among the highest strength alloys between 673K and 973K (752°F and 1292°F), the typical hot wall temperature range for rocket engine liners. Cold or warm working GRCop-84 can increase the yield strength to over 400 MPa (58 ksi) at room temperature.

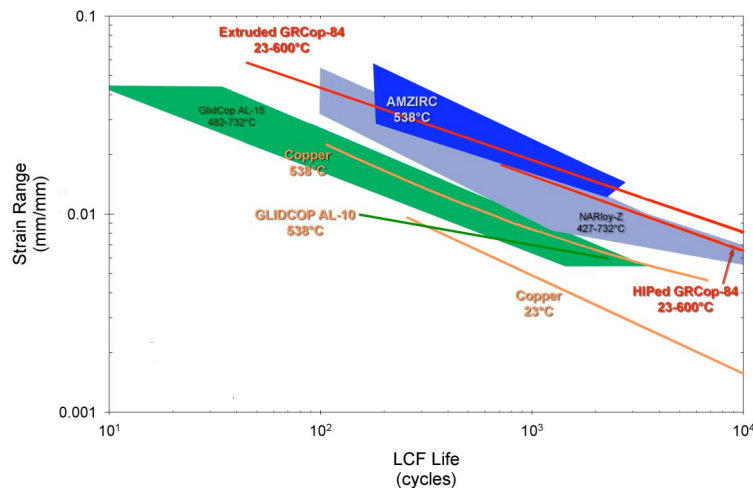


Figure 5 - Low Cycle Fatigue (LCF) is the primary property driving design of most liners for reusable launch vehicles (RLVs). It also plays an important role in expendable launch vehicle (ELV) engines as well. AMZIRC has a comparable LCF life, but GRCop-84 is clearly superior to NARloy-Z, GlidCOP and copper, in some cases by over an order of magnitude.

Component Testing

Vacuum plasma spraying has been used to make several small liners that have been hot fire tested for various durations at both NASA GRC and MSFC. One 9 kN (2,000 pound force) thrust cell tested had no protective coating and provides a baseline. The remaining liners had a NiCrAlY functional gradient material on the hot wall.

The uncoated liner test at NASA GRC accumulated 142 seconds of hot fire time during 11 hot fire tests lasting up to 30 seconds each. The mixture ratio (oxygen to hydrogen by weight) was limited to 7:1 to prevent blanching. Visual examination of the hot wall revealed no detectable changes to the surface.

Much more extensive testing of VPS liners with NiCrAlY functional graded material on the hot wall has been conducted by NASA MSFC. After the successful testing of a 9 kN coated thrust cell at NASA GRC that accumulated 340 seconds of hot fire testing in 17 hot fire tests, a 22 kN (5,000 pound force) thrust cell with a NiCrAlY functional gradient material hot wall was produced and tested. The liner underwent 108 hot firings with no visible degradation of the hot wall and no increase in heat transfer from surface roughening.

Summary

GRCop-84 has demonstrated stable mechanical properties at elevated temperatures that almost always are better than other high conductivity copper-based alloys especially after high temperature exposures. The alloy can be processed from powder using a variety of conventional, commercially available techniques. It has been demonstrated that GRCop-84 can be joined using friction stir welding, brazing, inertia welding, brazing, diffusion bonding and electron beam welding.

In total, GRCop-84 demonstrates a combination of a large variety of highly desirable mechanical and thermophysical properties that makes it a very attractive material to use at temperatures up to 700°C (1292°F).

Contact Information

If you wish more information, please contact Dr. David L. Ellis at the NASA Glenn Research Center.

Dr. David L. Ellis
NASA Glenn Research Center
21000 Brookpark Road
Cleveland, OH 44135-3127
Phone: 216-433-8736
FAX: 216-977-7132
E-mail: David.L.Ellis@nasa.gov

References

1. D.L. Ellis and G.M. Michal, Ultramicroscopy, Vol. 30, Nos. 1/2, pp. 210-216
2. D.L. Ellis and G.M. Michal, "Precipitation Strengthened High Strength, High Conductivity Cu-Cr-Nb Alloys Produced by Chill Block Melt Spinning," NASA CR-185144, NASA LeRC, Cleveland, OH, (Sept. 1989)
3. A. Adallah, G.M. Michal, D.L. Ellis, and J.J. Lewandowski, "Formability of a High Performance Dispersion Strengthened Cu-Cr-Nb Composite," Proc. Of 2003 Annual TMS Meeting
4. S. Elam, R. Holmes, T. McKechnie, R. Hickman, T. Pickens, **52nd JANNAF Propulsion Meeting/ 1st Liquid Propulsion Subcommittee Meeting**, Las Vegas, NV, May 2004.
5. R. Hickman, T. McKechnie, S. Elam and R. Holmes, **39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit**, Huntsville, AL, July 2003, AIAA paper 2003-4612.
6. S. Elam, J. Lee, R. Holmes, F. Zimmerman, **52nd International Astronautical Congress**, Toulouse, France, October 2001.
7. K.R. Anderson, J.R. Groza, R.L. Dreshfield, and D.L. Ellis, "High Performance Dispersion Strengthened Cu-8 Cr-4 Nb Alloy," Met. Trans A, Vol. 26A, (Sept. 1995), pp. 2197-2206.
8. T. Nagai, Z. Hanmi, and S. Koda, J. Japan Copper and Brass Assn., Vol. 14, (1975), pp. 60-73 (CDA Extract 13298).
9. T. Nagai, Z. Henmi, T. Sakamoto, and S. Koda, Trans. Japan. Inst. Metals. Vol. 14, No. 6, (Nov. 1973), pp. 462-469.
10. C. Russell, R. Carter, D. Ellis and R. Goudy, AIAA-2004-1995, 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference, Palm Springs, California, (Apr. 19-22, 2004)